Size resolved mass concentration and elemental composition of atmospheric aerosols over the eastern Mediterranean area

J. Smolik, V. ?dimal, J. Schwarz, M. Lazaridis, V. Havránek, K. Eleftheriadis, N. Mihalopoulos, C. Bryant, I. Colbeck

▶ **To cite this version:**

J. Smolik, V. ?dimal, J. Schwarz, M. Lazaridis, V. Havránek, et al.. Size resolved mass concentration and elemental composition of atmospheric aerosols over the eastern Mediterranean area. Atmospheric Chemistry and Physics Discussions, 2003, 3 (3), pp.2547-2573. hal-00301068

HAL Id: hal-00301068
https://hal.science/hal-00301068

Submitted on 19 May 2003

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Atmos. Chem. Phys. Discuss., 3, 2547–2573, 2003
www.atmos-chem-phys.org/acpd/3/2547/
© European Geosciences Union 2003

Atmospheric Chemistry and Physics Discussions

Size resolved mass concentration and elemental composition of atmospheric aerosols over the eastern Mediterranean area

J. Smolik[1], V. Ždimal[1], J. Schwarz[1], M. Lazaridis[3], V. Havránek[2], K. Eleftheriadis[4], N. Mihalopoulos[5], C. Bryant[6], and I. Colbeck[6]

[1]Institute of Chemical Process Fundamentals, ASCR, Prague, Czech Republic
[2]Nuclear Physics Institute AS CR, Prague, Czech Republic
[3]Technical University of Crete, Department of Environmental Engineering, 73100 Chania, Greece
[4]N. C. S. R. Demokritos, 15310 Ag. Paraskeui, Attiki, Greece
[5]Environmental Chemical Processes Laboratory (ECPL), Department of Chemistry, University of Crete 71409 Heraklion, Greece
[6]Department of Biological Sciences, University of Essex, UK

Received: 24 March 2003 – Accepted: 18 April 2003 – Published: 19 May 2003

Correspondence to: M. Lazaridis (lazaridi@mred.tuc.gr)

© EGU 2003

Abstract

A Berner low pressure impactor was used to collect size-segregated aerosol samples at Finokalia, located on the north-eastern coast of Crete, Greece during July 2000 and January 2001. Several samples were also collected during the summer campaign aboard the research vessel "AEGAIEO" in the Aegean Sea. Gravimetric analysis and inversion techniques yielded daily PM1 and PM10 mass concentrations. Further, the samples were analysed by PIXE giving elemental size distributions of Al, Si, K, Ca, Ti, Mn, Fe, Sr, S, Cl, Ni, V, Cu, Cr, Zn, and Pb. The crustal elements and sea-salt had a unimodal supermicron size distribution. Sulphur was found predominantly in submicron fractions. K, V, and Ni exhibited bimodal distribution with a submicron mode produced by forest fires and oil combustion. The anthropogenic elements had broad and not well-defined distributions. The time series for PM1 and PM10 mass and elemental concentrations showed both daily and seasonal variation. Higher mass concentrations were observed during two incursions of Saharan dust. Higher concentrations of S, Cu, Zn, and Pb were encountered in samples collected in air masses arriving from northern Greece or the western coast of Turkey. Higher concentrations of chlorine were found in samples with air masses either originating above the Atlantic Ocean and arriving at Finokalia via western Europe or recirculating over the western coast of the Black Sea.

1. Introduction

Intensive aerosol and gaseous pollutant measurement campaigns have been performed at Finokalia on the island of Crete (Greece) in combination with boat measurements in the eastern part of the Mediterranean area as part of the SUB-AERO project. The measurements were performed with the participation of 9 European research institutions. The above measurements together with regional/mesoscale/subgrid modelling studies were utilized to investigate the dynamics/characteristics of photochemical and fine particle pollutants in the Mediterranean area. The research work was performed

ACPD

3, 2547–2573, 2003

© EGU 2003

under the auspices of the European Union Fifth Framework Programme (project SUB-AERO).

Under this research framework gaseous phase measurements for a number of photo-oxidants, fine particle concentration measurements and detailed PM1 and PM10 particulate matter characterisation were carried out in the eastern Mediterranean area during summer 2000 and winter 2001. The experimental data were compared with modeling studies of the dynamics of photochemical gaseous species and particulate matter.

To the north of the Mediterranean Sea are the highly populated European countries with industrial, semi-industrial, and rural economies, whilst to the south is Africa. A detailed wind trajectory analyses shows that more than 60% of air masses which arrive in the eastern Mediterranean come from the N-NW and 13–16% from the Sahara (Guerzoni et al., 1990). Air masses from the N-NW contain particles related to industrial and urban inputs; those from Sahara carry predominantly mineral dust. Transport of Sahara dust occurs mostly during the spring and summer and causes non-continuous crustal aerosol pulses to the Mediterranean area (e.g. Bergametti et al., 1989b; Moulin et al., 1998). On the other hand, precipitation scavenging during the rainy season between October and May reduces aerosol concentrations (e.g. Dulac et al., 1987; Bergametti et al., 1989a). The summer time is also characterised by low-inversion layers, and strong sunlight, causing photochemical smog. Moreover, forest fires, which occur during the summer months in the Mediterranean region and in North Africa, increase black carbon and fine particle emissions. Thus, the Mediterranean Sea constitutes an area where atmospheric particles originating from continental natural and anthropogenic sources, marine sources and gas-to-particle conversion simultaneously exist. Furthermore, specific meteorological conditions result in high temporal variability of aerosol concentrations. Consequently, the Mediterranean area offers unique conditions for modelling/measurement studies.

Most of the studies on the chemical composition of Mediterranean particulate aerosol have been conducted in the western and north-western region (e. g. Dulac et al., 1987;

ACPD
3, 2547–2573, 2003

© EGU 2003

Bergametti et al., 1989a, b; Dulac et al., 1989; Migon et al., 1991; Migon et al., 1993; Sandroni and Migon, 1997) or on the eastern coast including Turkey and Israel (e. g. Mamane et al., 1980; Ganor et al., 1991; Kubilay et al., 1994; Luria et al., 1996; Maenhaut et al., 1999; Güllü et al., 2000; Yatin et al., 2000; Erduran and Tuncel, 2001). However relatively few studies have been undertaken in the southern part of the eastern Mediterranean and Greece (e.g. Chester et al., 1993; Mihalopoulos et al., 1997; Danalatos and Glavas, 1999; Chabas and Lefèvre, 2000). Here we report on the atmospheric aerosol measurement on the island of Crete (south-eastern Mediterranean) using cascade impactors and the characterisation of the collected particulate matter. Emphasis is placed on the mass and elemental size distributions and the temporal variability of PM1 and PM10.

2. Experimental

2.1. Sampling site

Aerosol samples were collected on Crete during the periods 10–31 July 2000 and 7–14 January 2001. According to analysis of 10 years air mass back trajectories (WMO, 1985; Guerzoni et al., 1990; Chester et al., 1993) 39% of air masses arrive at Crete from the north across Greece, eastern Europe and the former USSR, 28% of air masses arrive from the west-northwest, crossing western Europe, 16% come from the south, carrying with them aerosols from the Sahara and North Africa deserts, and 17% come from the east crossing the Middle East desert regions. Mihalopoulos et al. (1997) report similar figures. The main sampling site was located at Finokalia. Finokalia (35°19′ N, 25°40′ E) is a coastal remote site eastward Heraklion on the top a hill (~150 m a.s.l.) facing the sea within the sector of 270° to 90°. The sampling was carried out in open terrain about 3 m above the ground. In addition samples of atmospheric aerosol were also collected during the period 25–29 July 2000 aboard the research vessel “AEGAIEO”. The vessel cruised in the Aegean Sea along selected

© EGU 2003

tracks calculated by forward and back trajectory modelling with the Finokalia sampling site as the end point.

2.2. Sampling

Samples of atmospheric particulate matter were collected and size-segregated into 10 size fractions by two Berner type low pressure cascade impactors BLPI 25/0, 018/2, one from ICPF Prague and the second from "Demokritos", Athens. The impactors were used alternately at Finokalia station during the period 10–19 July 2000. After that the measurements at Finokalia continued with an impactor from Prague and the impactor from "Demokritos" was used aboard the "AEGAION" vessel. Both impactors were used alternately during the winter campaign (7–14 January 2001). In order to determine the real cut diameters and shapes of collection efficiency curves the impactor from Prague was calibrated at the Finnish Meteorological Institute by the method described by Hillamo and Kauppinen (1991). It was found that real cut diameters (D_{50} values) for stages 1–10 were 0.026, 0.062, 0.110, 0.173, 0.262, 0.46, 0.89, 1.77, 3.4, and 6.8 μm. Further, it was found that all stages of impactor have reasonably sharp collection efficiency curves, which makes the impactor response suitable for use with a data inversion technique (Hillamo et al., 1999). Before both campaigns the impactors were compared during 2-day measurements of mass size distribution of urban aerosol in Athens. For this purpose both impactors were connected in parallel to the same vacuum pump and two 24-hour samples were taken. The result of intercomparison is shown in Fig. 1, where D_{ae} is the geometric mean aerodynamic diameter. As can be seen the instruments were practically identical.

The sampling at Finokalia was carried out on the roof of small building. The impactor, with an inlet providing approximately 15 μm upper cut-off particle size, was positioned at a height of about 3 m above the ground. To reduce particle bounce the samples were deposited on Nuclepore polycarbonate foils greased with Apiezon L vacuum grease. Sampling was carried out in approximately 24-hour intervals with a flow rate of 25 l/min (in some cases the real time was shorter due to electrical current interruptions). The

© EGU 2003

first sample was taken from 10 July 2000, 10:00 to 11 June 2000, 10:00 local time. Due to some technical problems samples on the boat were not taken at standard times, as at the Finokalia, and sampling times were usually shorter. In total 5 samples were collected aboard the boat over the following time intervals 25 July (23:10)–26 July (09:53), 26 July (11:15)–27 July (10:20), 27 July (11:12)–28 July (09:15), 28 July (10:45)–29 July (01:15), and on 29 July between 09:00–18:43. During the winter sampling started at about 14:00. Thus the first sample was taken between 7 January 2001 (14:00) and 8 January 2001 (14:00). In total 21 samples from the summer campaign, 5 samples from the boat and 7 samples from the winter measurements were obtained, with each sample consisting of 10 size fractions.

2.3. Gravimetric analysis

The mass size distributions were obtained from the mass of particulate matter deposited on the individual stages of the impactor, volume flow rate of aerosol and total time of sampling. The electronic microbalances ATTA Cahn and Sartorius BP211D with a maximum attainable precision of 10 μg were used for weighing the aerosol samples from the summer campaign. During the winter campaign Sartorius M5P-000V001 electronic microbalances with maximum attainable precision of 1 μg were used. Foils were transported from the sampling site in Petri dishes and equilibrated in the weighing room for at least 24 hours before weighing at conditions R.H. 56 ± 13% and temperature 24.7 ± 1.0° C (summer), R.H. 62.8 ± 2.5% and temperature 26.8 ± 1.0° C (boat) and R.H. 69.2 ± 1.8 and temperature 21.4 ± 0.8 (winter). Internal calibration of the balance was performed regularly, at least once at the beginning of each weighing run. To check reproducibility of the weighing procedure, a control aluminum foil was weighed at least once during each weighing run. Before and after each weighing run another control substrate (blank made of the same polycarbonate foil processed the same way but without a sample) was weighed to check the influence of possible temperature and RH fluctuations.

ACPD
3, 2547–2573, 2003

© EGU 2003

2.4. Elemental analysis

All samples were analysed by particle-induced X-ray emission (PIXE). Analyses were performed on the 3 MeV Van de Graaff electrostatic accelerator at the Nuclear Physics Institute in Řež at Prague. The samples consisted of annular deposit of individual spots, with number of spots depending on the stage. The 8 mm collimator of proton beam for stage 1 and 3 mm collimator for stages 2–10 were used. Usually, 6 spots from stage 1, 2 spots from stage 2, and 1 spot from stages 3–10 were analysed. To obtain the elemental concentrations for individual size fractions deposited on impaction foils, the results of analysis was related to the actual number of spots on each stage. Two proton beam energies of 1.31 MeV and 2.35 MeV were used to irradiate samples. Usually the proton fluence of about 10 μC and 50 μC were used for the 1.31 MeV and 2.35 MeV measurement, respectively. The typical time for one irradiation was about 5 min. The 1 mm polyethylene absorption filter was used for the 2.35 MeV irradiation to reduce the intensive low energy X-rays from sample. In samples from the summer campaign Al, Si, K, Ca, Ti, Mn, Fe, Sr, S, Cl, Ni, V, Cu, Cr, Zn, and Pb were determined. During the winter campaign a new set of polycarbonate foils with low blank of Br was used. This allowed the determination of Br in the samples. Elements up to Ti were determined from 1.31 MeV while the rest of elements from the 2.35 MeV measurement. The influence of the observed matrix effect due to the deposit thickness was corrected using the Equivalent Layer Thickness Model (Havránek et al., 1999). The ratio of the Fe signal from 1.35 MeV and 2.35 MeV irradiation was used to estimate the effective thickness of aerosol deposit for individual spots.

ACPD

3, 2547–2573, 2003

© EGU 2003

3. Results and discussion

3.1. Mass size distributions

A total of 21 mass size distributions from the summer campaign, 5 mass size distributions from the boat and 7 mass size distributions from the winter measurements were obtained. The distributions were predominantly bimodal with mode mean diameters around 0.4 and 5 μm and with minimum between both modes at around 1 μm. The raw mass size data were inverted into smooth mass size distributions by the MICRON code (Wolfenbarger and Seinfeld, 1990). The inverted distributions were integrated to obtain PM1 and PM10 mass concentrations. The time series of PM1 and PM10 for both summer and winter campaigns are shown in Fig. 2. As can be seen PM1 and PM10 mass concentrations show both short-term (daily) and long-term (seasonal) variations. In our case the daily PM10 mass concentration, measured at Finokalia during the summer, ranged from 20.7 to 40 μg/m^3 (10–18 July 2000), after that it was practically constant being approximately 29 μg/m^3 (19–25 July 2000) before increasing up to 67.2 μg/m^3 (27 July 2000) and finally decreasing to 37 μg/m^3 (30 July 2000). A similar increase of PM10 concentration was observed in samples collected aboard the boat, with a maximum of 75.1 μg/m^3 (28 July 2000). The daily PM1 mass concentration, measured during the summer, ranged from 3.7 to 20.2 μg/m^3 and from 11.6 to 25.9 μg/m^3 at Finokalia and aboard the boat, respectively. During the winter the daily PM1 and PM10 concentrations varied from 2.4 to 8.6 μg/m^3 and from 10.1 to 19.5 μg/m^3, respectively. The short-term variation in aerosol mass and composition, is observed frequently in the Mediterranean area and surrounding regions. It is caused mainly by changes in air mass transport arriving from different sectors toward the sampling point (e.g. Dulac et al., 1987; Bergametti et al., 1989a, b, 1992; Guerzoni et al., 1990; Ganor et al., 1991; Hacisalihoglu et al., 1991, 1992; Migon et al., 1993; Kubilay et al., 1994, 1995; Luria et al., 1996; Mihalopoulos et al., 1997; Sandroni and Migon, 1997; Güllü et al., 2000; Danalatos and Glavas, 1999; Chabas and Lefèvre, 2000; Yatin et al., 2000; Erduran and Tuncel, 2001).

ACPD
3, 2547–2573, 2003

© EGU 2003

To estimate the effect of air mass transport we computed the backward trajectories (HYSPLIT4 Trajectory Model with 6 h time steps 72 h backward in time for two transport layers 300–2000 m and 1500–3000 m). The results showed that the air masses arriving in Crete changed direction several times between north and west during the first period (10–18 July 2000). Higher PM10 concentrations were observed with air masses originating over the Atlantic Ocean and western Europe (10, 13, and 16 July 2000). The relatively constant PM10 concentration observed during 19–25 July 2000 corresponded to air masses originating from the area of western coast of the Black Sea. The peak PM10 mass concentrations, observed during the end of the summer campaign, corresponded to air masses from North Africa. During the winter campaign higher mass concentrations were observed with air masses originatinating over the Atlantic Ocean and arriving via Northern Africa and the Mediterranean Sea (9 January 2001). Higher mass concentrations were also observed with air masses originatinating from southern Greece and the Ionian Sea, that recirculated above Crete (7 January 2001) or originated above the Mediterranean Sea and recirculated above the North Africa coast. However, for similar meteorological conditions low aerosol mass concentrations were also found (8 January 2001).

The long-term (seasonal) variation results in different average aerosol concentrations observed during the different seasons. In our case the geometric mean PM1 and PM10 mass concentrations, measured at Finokalia during the summer, were 11.44 and 32.09 μg/m^3, respectively. Corresponding winter mass concentrations were 4.22 and 14.17μg/m^3, respectively. Similar seasonal variability of aerosol concentrations in the Mediterranean region was observed by other authors (e. g. Bergametti et al., 1989a, b; Güllü et al., 2000; Chabas and Lefèvre, 2000). This may be attributed to the scavenging by precipitation during transport from source areas that is more frequent during the rainy period in autumn and winter.

ACPD
3, 2547–2573, 2003

© EGU 2003

3.2. Elemental size distributions

As already mentioned in previous paragraphs Al, Si, K, Ca, Ti, Mn, Fe, Sr, S, Cl, Ni, V, Cu, Cr, Zn, and Pb were determined in the BLPI samples using PIXE. In addition a new set of polycarbonate foils with low blank of Br was used during the winter campaign that allowed Br to be determined. Typically samples collected on stages 1–6 (i.e. with particles < 1 μm in diameter) were black indicating the presence of soot from combustion. The samples with coarse particles were beige in colour corresponding to mineral dust. Principally three types of elemental size distribution were observed. A monomodal distribution with particle size > 1 μm and mode centered at about 4μm was typical for Al, Si, Ca, Ti, Mn, Fe, and Sr. Also Cl exhibited a monomodal distribution with particle size > 1 μm and mode around 5 μm. S, Br, K, V, and Ni exhibited bimodal distributions with modes around 0.3 and 3 μm and minimum at about 1 μm. Cu, Cr, Zn, and Pb showed rather flat multimodal distributions centered at approximately 1 μm. The raw elemental size data were inverted into smooth elemental size distributions by the MICRON code and the inverted distributions were integrated to obtain PM1 and PM10 elemental concentrations. Geometric mean mass and elemental concentrations in PM1 and PM10 fractions of atmospheric aerosols collected at Finokalia during the summer and winter campaigns are compared in Table 1. As can be seen the winter values are considerably lower except for Cl. Further, Table 2 shows comparison of mass and elemental concentrations in PM1 and PM10 aerosols collected during corresponding days at Finokalia and aboard the "AEGAIEO" vessel. Both mass and elemental concentrations found at Finokalia and aboard the vessel are comparable with the exception of Cl, V, and Ni.

In addition the PM10 mass and elemental concentrations, determined from 21 summer samples collected at Finokalia were used in principal component analysis (Varimax rotated factor analysis) to identify possible sources of individual elements. The results are given in Table 3. The first factor contains the group of crustal elements Ca, Al, Fe, Mn, K, Ca, Ti, Cr and Sr and explains 39% of the total system variance. The sec-

ACPD
3, 2547–2573, 2003

© EGU 2003

ond factor, mainly associated with Cl, represents the marine factor and explains 19% of the variance. Thus cumulative variance from crustal and marine influence explain up to 60% of the variability indicating greater influence of natural sources compared to anthropogenic ones in the region. The third factor includes Pb, S, Cu and Zn and is attributed to pure anthropogenic sources. Finally the last factor contains V and Ni having mixed origin from both anthropogenic and crustal sources. As can be seen the results of factor analysis agree fairly well with the individual elemental size distributions. Coarse modes observed for crustal elements and chlorine correspond to mineral dust and sea-salt particles produced by bursting of bubbles. The size distribution of sulphur, where the accumulation mode dominates, shows that particulate sulphur is mainly a product of gas-to-particle conversion (Finlayson-Pitts and Pitts, 2000). Bimodal distributions for K, Ni, and V indicate that these elements are both anthropogenic and natural in origin. Potassium in submicrometer particles results from biomass burning, nickel and vanadium come from oil combustion. Rather broad distributions of Cu, Cr, Zn and Pb with not too well-defined peaks indicate more sources and an aged aerosol.

The next figures show the temporal variation of PM1 and PM10 for several elements characteristic for individual groups of elements as found from factor analysis and also for different types of the above mentioned elemental size distributions. Figure 3a shows the time series of PM1 and PM10 for Si as a typical crustal element. As can be seen PIXE revealed another peak in concentration of Si on 12 July 2000. According to backward trajectories and Meteosat pictures this increase was caused by Saharan dust. Figure 3b shows the temporal variation of another crustal element potassium, which exhibited a bimodal distribution. Here the higher concentrations correspond both to Saharan dust, where the potassium is present in illite (e.g. Ganor et al., 1991; Molinaroli, 1996), and to forest fires. This follows from satellite pictures showing forest fires in Greece and surrounding areas that occurred at the beginning of summer campaign, and from higher concentrations of potassium in the PM1 fraction found in the corresponding samples. The latter is typical for wood combustion (e. g. Valmari et al., 1998) and biomass burning (e. g. Jaffrezo et al., 1998). Figure 3c shows the temporal varia-

ACPD
3, 2547–2573, 2003

© EGU 2003

tion of chlorine. For chlorine we have not observed any specific dependence on the air mass trajectories, but rather on the velocity of air mass transport. Higher chlorine concentrations were observed for air masses which originated over the Atlantic Ocean and were transported with a higher velocity across Europe (10, 13–17 July 2000, 9 and 10 January 2001) or originated above the western coast of the Black Sea (20 and 21 July 2000). Low chlorine concentrations were found for calm days. The origin of chlorine in atmospheric aerosol is mainly sea-salt particles produced by bursting of air bubbles at the ocean surface. The number of sea-salt particles depends approximately exponentially on the wind speed (Lovett, 1978; Monahan et al. 1986; Smith et al. 1993). This shows the exponential dependence of marine elements concentrations on the local wind speed observed in the Mediterranean area (e.g. Bergametti et al., 1989a; Chabas and Lefèvre, 2000). Since, we have not found any correlation with the local wind speed the observed chlorine concentrations depend on distant marine source strength and long range transport to Crete, and that both should be also related to the wind speed. Figure 3d shows the behaviour of sulphur. As can be seen sulphur was predominantly found in submicron particles. Concentrations of sulphur determined in the PM1 and PM10 fractions by PIXE were well correlated with the concentrations determined in the soluble fraction by ion chromatography (Bardouki et al., 2002) with a slope of unity. It shows that sulphur was present as sulphate. Lower concentrations were observed for air masses which originated over the Ligurian Sea and the Mediterranean Sea to the west of Crete. Higher concentrations were observed for air masses arriving from the west coast of the Black Sea or from the west Europe but recirculated later above the west coast of the Black Sea and arriving from the North. Figure 3d also shows the seasonal variation in sulphur, with higher concentrations being observed in the summer. This is in agreement with other results from this region (Tsitouridou and Samara, 1993; Luria et al., 1996; Mihalopoulos et al., 1997; Danalatos and Glavas, 1999). Higher sulphate concentrations in the summer may be caused by higher phytoplanktonic activity producing gaseous dimethylsulphide that is later oxidised to methanesulphonic acid and sulphur dioxide (Finlayson-Pitts and Pitts, 2000) and larger conversion rates due

© EGU 2003

to higher concentrations of oxidising species (Danalatos and Glavas, 1999).

As found earlier at Finokalia, the biogenic sulphur can account for 0.6 to 28.3% of the total non-sea sulphate concentrations (Mihalopoulos et al., 1997) with higher values observed during the summer. Also the long range transport of sulphates may have greater influence in summer due to rare precipitation events in the region during this period (Luria et al., 1996). In our case the non-sea sulphate concentrations followed the ^{222}Rn variation and this indicates air of continental origin (Bardouki et al., 2002). This can be supported by the similar behaviour of time series found for sulphur and anthropogenic elements Cu, Pb, and Zn. The temporal variation of vanadium is shown in Fig. 3e. As found from factor analysis vanadium should have mixed origin, it is produced by the fuel oil combustion, but it is also by crustal elements (Finlayson-Pitts and Pitts, 2000). As a result vanadium is found both in submicron and coarse particles. The effect of the oil combustion is clearly seen from the high concentration of vanadium found aboard the boat, coming from oil driven engines of both the "AEGAIEO" and other vessels cruising in the area. Also vanadium in Saharan dust increased its concentration towards the end of the summer campaign (Schütz and Rahn, 1982; Bonelli et al., 1996).

It follows that the atmospheric input of trace elements into the central and eastern Mediterranean is a complex phenomenon that depends on the transport of pollutants from their sources. This includes air mass movement, strength and spatial distribution of sources, precipitation scavenging by distant and local rain events, and for some elements such as halogens even on chemical reactions. Thus, it is very difficult to generalize and continuing long-term measurements of size- and time resolved chemical composition of atmospheric particles is needed.

4. Conclusions

Size resolved aerosol samples were collected at Finokalia, a coastal site in Crete and aboard the research vessel "AEGAIO" cruising the Aegean Sea during two periods in July 2000 and January 2001. Gravimetric analysis of samples yielded PM1 and PM10

© EGU 2003

temporal variations. The elemental composition of samples was determined by PIXE. The time series for PM1 and PM10 showed both daily and seasonal variation. The daily variation was caused mainly by air masses arriving at Crete from different directions including two incursions of Saharan dust. The seasonal variation was probably caused by precipitation scavenging, which is more frequent in winter. The elemental analysis showed practically monomodal distributions for crustal elements, chlorine, and sulphur. Sulphur has most of its mass in the submicron size range, crustal elements and chlorine in the supermicron fractions. Three elements K, V, and Ni, which have both anthropogenic and crustal origin, exhibited bimodal distributions. Higher concentrations of potassium in submicron particles corresponded to forest fires, and vanadium and nickel to the oil combustion. High concentrations of vanadium and nickel in submicron particles, produced probably by oil driven engines of both "AEGAION" and other vessels, was found in samples collected aboard the boat. Anthropogenic elements Cr, Cu, Pb, and Zn exhibited broad and not too well-defined distributions. Higher concentrations of these elements were found for air masses originating from the west coast of the Black Sea and advected across northern Greece and western Turkey. The time series for Cu, Pb, and Zn, resemble behaviour of sulphur that indicates a similar source.

Acknowledgement. The authors gratefully acknowledge the help of G. Kouvarakis in factor analysis. This work was supported by the European Commission under grant ENVK2-1999-00052.

References

Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Ždimal, V., Eleftheriadis ,K., Lazaridis, M., and Mihalopoulos, N.: Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter, Atmospheric Environment, 37, 195–208, 2003.

Bergametti, G., Dutot, A.-L., Buat-Ménard, P., Losno, R., and Remoudaki, E.: Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean, Tellus, 41B, 353–361, 1989a.

© EGU 2003

Bergametti, G., Gomes, L., Remoudaki, E., Desbois, M., Martin, D., and Buat-Ménard, P.: Present transport and deposition patterns of African dust to the North-Western Mediterranean, in: Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport (Leinen, M. and Sarthein, M., eds.), Kluwer Academic Publishers, Dordrecht, 227–252, 1989b.

Bonelli, P., Braga Marcazzan, G. M., and Cereda, E.: Elemental composition and air trajectories of African dust transported in northern Italy, in The Iimpact of Desert Dust Across the Mediterranean (Guerzoni, S. and Chester, R., eds.), Kluwer Academic Publishers, Dordrecht, 275–283, 1996.

Chabas, A. and Lefèvre, R. A.: Chemistry and microscopy of atmospheric particulates at Delos (Cyclades-Greece), Atmospheric Environment, 34, 225–238, 2000.

Chester, R., Nimmo, M, Alarcon, M., Saydam, C., Murphy, K. J. T., Sanders, S. G., and Corcoran, P.: Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions, Oceanologica Acta, 16, 231–246, 1993.

Danalatos, D. and Glavas, S.: Gas phase nitric acid, ammonia and related particulate matter at a Mediterranean coastal site, Patras, Greece, Atmospheric Environment, 33, 3417–3425, 1999.

Dulac, F., Buat-Ménard, P., Arnold, M., Ezat, U., and Martin, D.: Atmospheric input of trace metals to the western Mediterranean Sea: 1. Factors controlling the variability of atmospheric concentrations, J. Geophys. Res., 92, 8437–8453, 1987.

Dulac, F., Buat-Ménard, P., Ezat, U., and Melki, S.: Atmospheric input of trace metals to the western Mediterranean: uncertainties in modelling dry deposition from cascade impactor data, Tellus 41B, 362–378, 1989.

Erduran, M. S. and Tuncel, S. G.: Gaseous and particulate air pollutants in the northeastern Mediterranean Coast, Sci. Total Environ., 281, 205–215, 2001.

Finlayson-Pitts, B. J. and Pitts, J. N., Jr.: Chemistry of the Upper and Lower Atmosphere, Theory, Experiments, and Applications, Academic Press, San Diego, 2000.

Ganor, E., Foner, H. A., Brenner, S., Neeman, E., and Lavi, N.: The chemical composition of aerosols settling in Israel following dust storms, Atmospheric Environment, 25A, 2665–2670, 1991.

Guerzoni, S., Correggiari, I., and Miserocchi, S.: Wind-blown particles from ships and land-based stations in the Mediterranean See: A review of trace metal sources, Water Poll. Res. Rep., 20, 377–386, 1990.

© EGU 2003

Güllü, G., Ölmez, I., and Tuncel, G.: Temporal variability of atmospheric trace element concentrations over the eastern Mediterranean Sea, Spectrochimica Acta B, 55, 1135–1150, 2000.
Hacisalihoglu, G., Balkas, T. I., Tuncel, S. G., Herman, D. H., Ölmez, I., and Tuncel, G.: Trace element composition of the Black Sea aerosols, Deep-Sea Res., 38, S1255–S1266, 1991.
Hacisalihoglu, G., Eliyakut, F., Ölmez, I., Balkas, T. I., and Tuncel, G.: Chemical composition of particles in the Black Sea atmosphere, Atmospheric Environment, 26A, 3207–3218, 1992.
Havránek, V., Kucera, J., Horáková, J., Vosecek, V., Smolik, J., Schwarz, J., and Sýkorová, I.: Matrix effects in PIXE analysis of aerosols and ashes, Biological Trace Elements Research, 71–72, 431–442, 1999.
Hillamo, R. E. and Kauppinen, E. I.: On the performance of the Berner low pressure impactor, Aerosol Sci. Technol., 14, 33–47, 1991.
Hillamo, R. E., Makela, T., Schwarz, J., and Smolik, J.: Collection characteristics of the model 25/0, 018/2 Berner low pressure impactor, J. Aerosol Sci., 30, S1, 901–902, 1999.
Jaffrezo, J. L., Davidson, C. I., Kuhns, H. D., Bergin, M. H., Hillamo, R., Maenhaut, W., Kahl, J. W., and Harris, J. M.: Biomass burning signatures in the atmosphere of central Greenland, J. Geophys. Res., 103, 31 067–31 078. 1998.
Kubilay, N., Yemenicioglu, S., and Saydam, C.: Trace metal characterization of airborne particles from the northeastern Mediterranean, Fresenius Envir. Bull., 3, 444–448, 1994.
Kubilay, N., Yemenicioglu, S., and Saydam, C.: Airborne material collections and their chemical composition over the Black Sea, Marine Pollution Bull., 30, 475–483, 1995.
Lovett, R. F.: Quantitative measurements of airborne sea-salt in the north Atlantic, Tellus, 30, 358–363, 1978.
Luria, M., Peleg, M., Sharf, G., Tov-Alper, D. S., Spitz, N., Ben Ami, Y., Gawii, Z., Lifschitz, B., Yitzchaki, A., and Seter, I.: Atmospheric sulfur over the east Mediterranean region, J. Geophys. Res., 101, 25 917–25 930, 1996.
Maenhaut, W., Ptasinski, J., and Cafmeyer, J.: Detailed mass size distributions of atmospheric aerosol species in the Negev desert, Israel, during ARACHNE-96, Nucl. Instrum. Meth. B, 150, 422–427, 1999.
Mamane, Y., Ganor, E., and Donagi, A. E.: Aerosol composition of urban and desert origin in the Eastern Mediterranean, I. Individual particle analysis, Water Air Soil Pollut., 14, 29–43, 1980.
Migon, C., Morelli, J., Nicolas, E., and Copin-Montegut, G.: Evolution of total atmospheric

© EGU 2003

deposition of Pb, Cd, Cu and Zn to the Ligurian Sea, Sci. Total Environ., 105, 135–148, 1991.
Migon, C., Alleman, L., Leblond, N., and Nicolas, E.: Evolution of atmospheric lead over the northwestern Mediterranean between 1986 and 1992, Atmospheric Environment, 27A, 2161–2167, 1993.
Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bosquet, P.: Tropospheric aerosol ionic composition in the Eastern Mediterranean region, Tellus, 49B, 314–326, 1997.
Molinaroli, E.: Mineralogical characterisation of Saharan dust with a view of its final destination in Mediterranean sediments, In The Impact of Desert Dust Across the Mediterranean (Guerzoni, S. and Chester, R., eds,), Kluwer Academic Publishers, Dordrecht, 153–162, 1996.
Monahan, E. C., Spiel, D., and Spiel, K.: Oceanic whitecaps, Reidel, 1986.
Moulin, C., Lambert, C. E., Dayan, U., Masson, V., Ramonet, M., Bousquet, P., Legrand, M., Balkanski, Y. J., Guelle, W., Marticorena, B., Bergametti, G., and Dulac, F.: Satellite climatology of African dust transport in the Mediterranean atmosphere, J. Geophys. Res., 103, 13 137–13 144, 1998.
Sandroni, V. and Migon, C.: Significance of trace metal medium-range transport in the western Mediterranean, Sci. Total Environ., 196, 83–89, 1997.
Schütz, L. and Rahn, K. A.: Trace-element concentrations in erodible soil, Atmospheric Environment, 16, 171–176, 1982.
Smith, M. H., Park, P. M., and Consterdine, I. E.: Marine aerosol concentration and estimated fluxes over seas, Q. J. R. Meteorol. Soc., 809–824, 1993.
Tsitouridou, R. and Samara, C.: First results of acidic and alkaline constituents determination in air particulates of Thessaloniki, Greece, Atmospheric Environment, 27B, 313–319, 1993.
Valmari, T., Kaupinnen, E. I., Kurkela, J., Jokiniemi, J. K., Sfiris, G., and Revitzer, H.: Fly ash formation and deposition during fludized bed combustion of willow, J. Aerosol Sci., 29, 445–459, 1998.
Wolfenbarger, J. K. and Seinfeld, J.K.: Inversion of aerosol size distribution data, J. Aerosol Sci., 21, 227–247, 1990.
World Meteorological Organization: Atmospheric transport of contaminants into the Mediterranean region, GESAMP Report and Studies, 26, 53, 1985.
Yatin, M., Tuncel, S., Aras, N. K., Ölmez, I., Aygün, S., and Tuncel, G.: Atmospheric trace elements in Ankara, Turkey: 1. factors affecting chemical composition of fine particles, Atmospheric Environment 23, 1305–1318, 2000.

© EGU 2003

Table 1. Geometric mean mass ($\mu g/m^3$) and elemental (ng/m^3) concentrations in PM1 and PM10 fractions of atmospheric aerosol collected at Finokalia during the summer (10–31 July 2000) and winter (7–14 January 2001) campaigns

	PM1		PM10	
	Summer	Winter	Summer	Winter
Mass	11	4	32	14
Al	44	27	251	99
Si	130	69	1106	257
S	1837	575	2167	740
Cl	0	6	724	825
K	81	78	269	138
Ca	21	7	549	153
Ti	2	0	22	2
V	4	2	6	3
Cr	0	0	1	0
Mn	1	0	6	1
Fe	19	5	246	34
Ni	1	1	2	2
Cu	0	0	2	1
Zn	6	2	10	3
Sr	0	0	2	1
Pb	8	3	12	6
Br	nd	3	nd	5

ACPD
3, 2547–2573, 2003

© EGU 2003

Table 2. Geometric mean mass ($\mu g/m^3$) and elemental (ng/m^3) concentrations in PM1 and PM10 fractions of atmospheric aerosol collected at Finokalia station and aboard the research vessel "AEGAIEO" during 25–29 July 2000

	PM1		PM10	
	Finokalia	Vessel	Finokalia	Vessel
Mass	17	20	46	53
Al	39	35	496	426
Si	294	167	2866	2838
S	2705	2703	2913	3043
Cl	0	0	155	417
K	109	87	455	468
Ca	62	25	1093	896
Ti	9	6	79	87
V	7	13	11	18
Cr	1	1	1	1
Mn	2	2	16	16
Fe	80	51	800	828
Ni	2	6	3	7
Cu	1	1	2	2
Zn	9	10	15	20
Sr	0	0	5	4
Pb	10	13	16	20
Br	nd	nd	nd	nd

ACPD
3, 2547–2573, 2003

© EGU 2003

Table 3. Factor loadings of concentrations of elements in PM10 particulate matter

Factor isolated	Factor 1	Factor 2	Factor 3	Factor 4
Mass	0.799	0.038	0.392	0.309
Sr	0.961	0.110	0.010	0.135
Si	0.959	−0.133	0.183	0.125
Al	0.953	−0.082	0.087	−0.024
Fe	0.953	−0.147	0.160	0.176
Ti	0.953	−0.140	0.133	0.205
K	0.928	0.068	0.287	0.037
Mn	0.927	−0.175	0.234	0.183
Ca	0.926	0.023	0.259	0.080
Cr	0.730	0.019	0.285	0.117
V	0.670	−0.139	0.342	0.603
Ni	0.544	−0.093	0.265	0.755
Cl	−0.237	0.812	−0.343	−0.137
Pb	0.133	−0.103	0.925	0.017
Cu	0.355	0.125	0.880	−0.060
S	0.284	−0.207	0.841	0.164
Zn	0.190	−0.265	0.791	0.234
Eigenvalues	9.87	4.63	5.16	2.01
Fractional variance	0.39	0.19	0.21	0.08

ACPD
3, 2547–2573, 2003

© EGU 2003

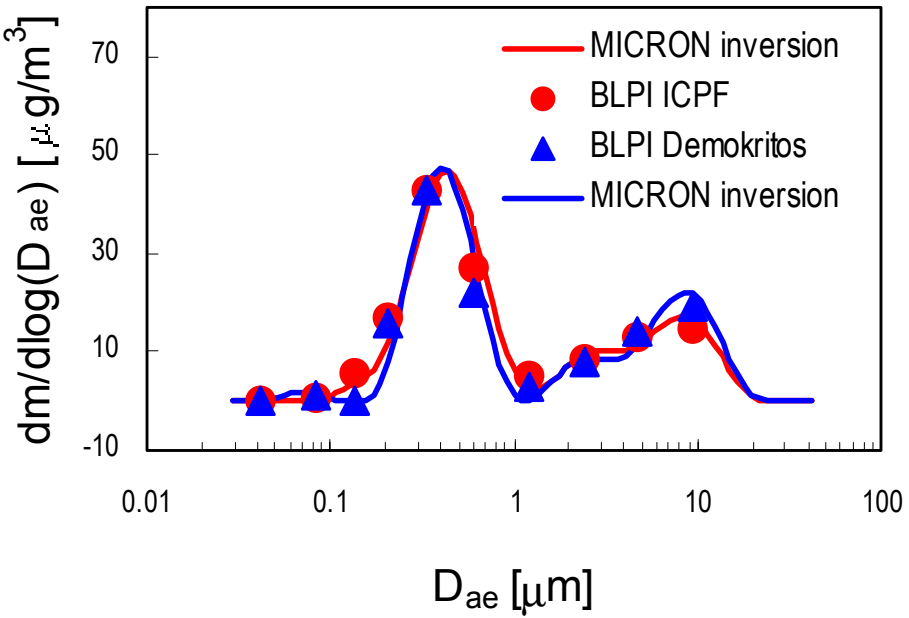

Fig. 1. Intercomparison of two BLPI cascade impactors. The raw mass size data were inverted into smooth mass size distributions by the MICRON code.

ACPD
3, 2547–2573, 2003

© EGU 2003

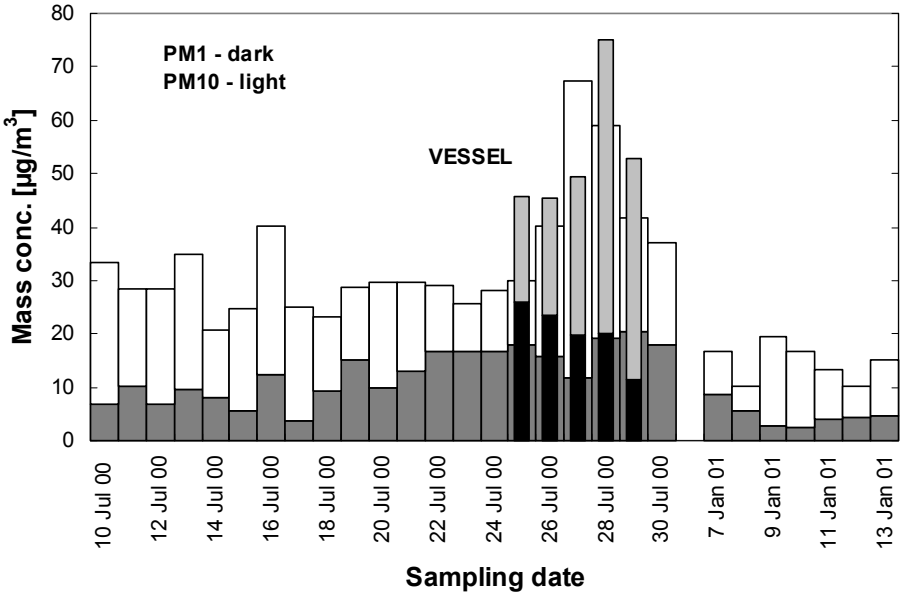

Fig. 2. Daily PM1 and PM10 mass concentrations at Finokalia and aboard the research vessel "AEGAIEO".

ACPD
3, 2547–2573, 2003

© EGU 2003

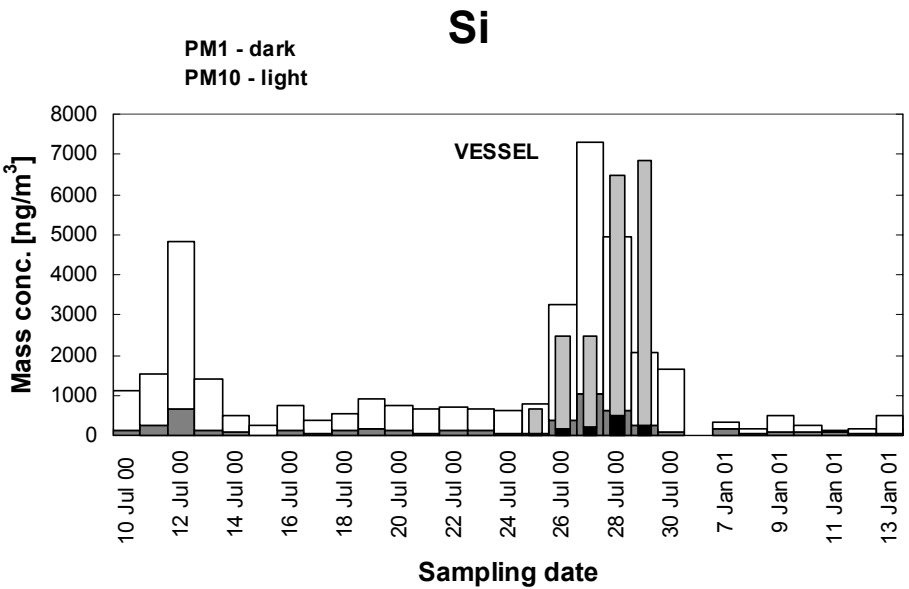

Fig. 3. **(a)** Daily concentrations of **(a)** Si, **(b)** K, **(c)** Cl, **(d)** S, and **(e)** V in PM1 and PM10 at Finokalia and aboard of the research vessel "AEGAIEO".

ACPD
3, 2547–2573, 2003

© EGU 2003

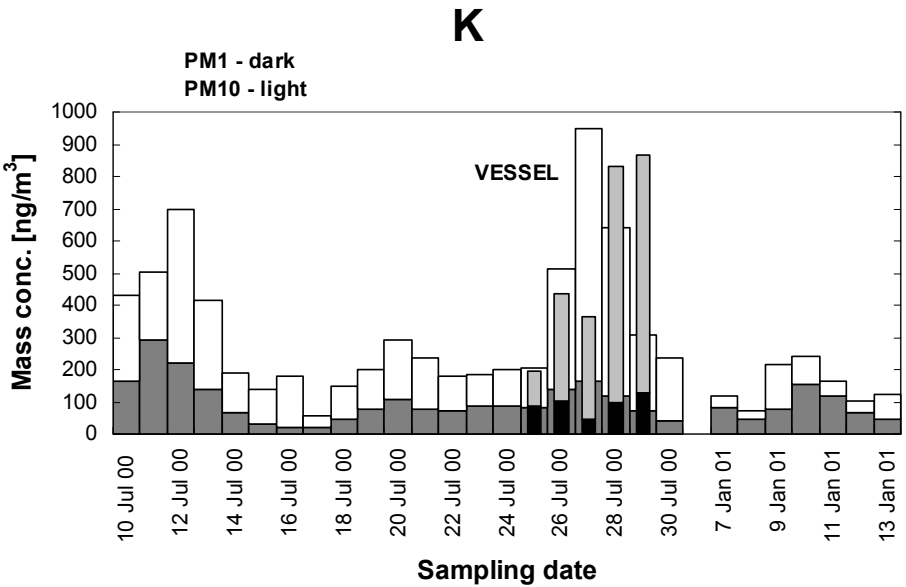

Fig. 3. (b) Continued.

ACPD
3, 2547–2573, 2003

© EGU 2003

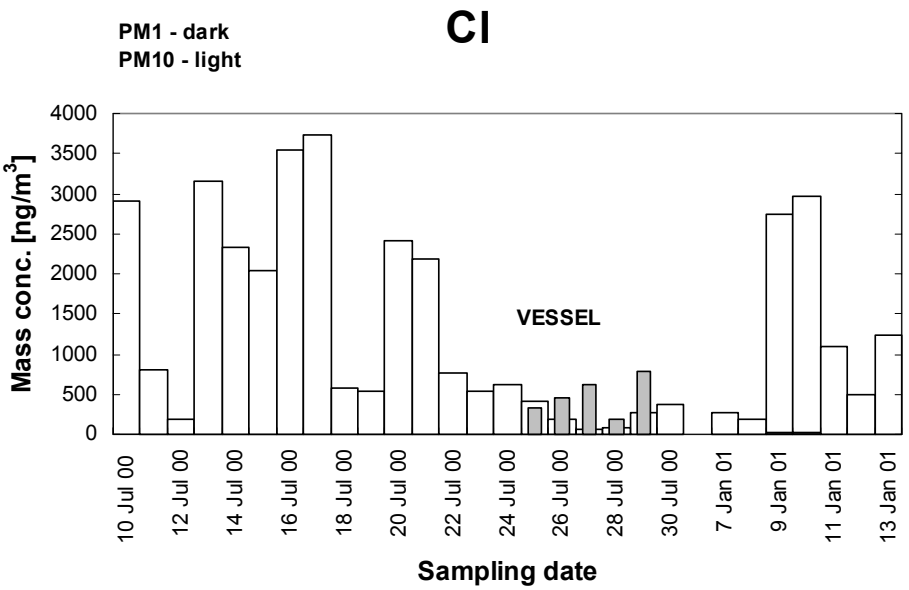

Fig. 3. (c) Continued.

ACPD
3, 2547–2573, 2003

© EGU 2003

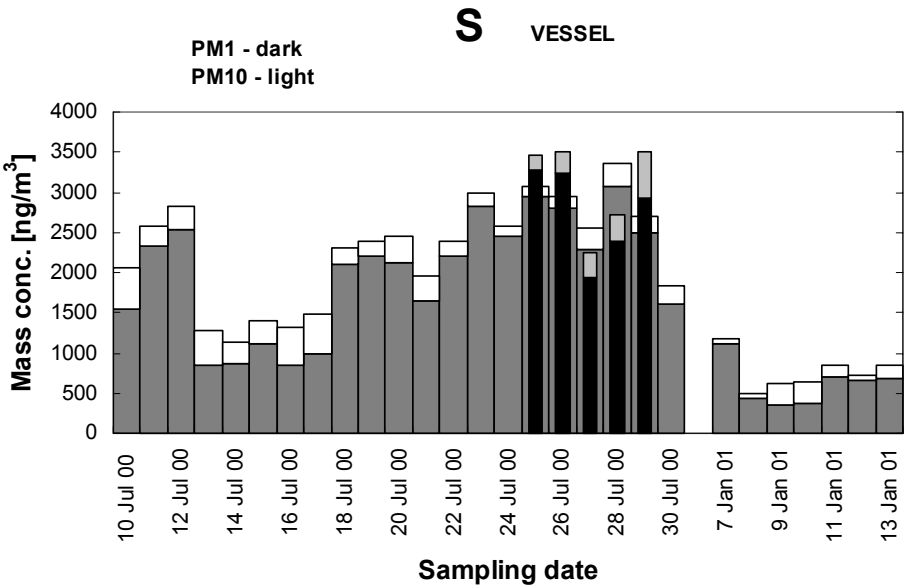

Fig. 3. (d) Continued.

ACPD
3, 2547–2573, 2003

© EGU 2003

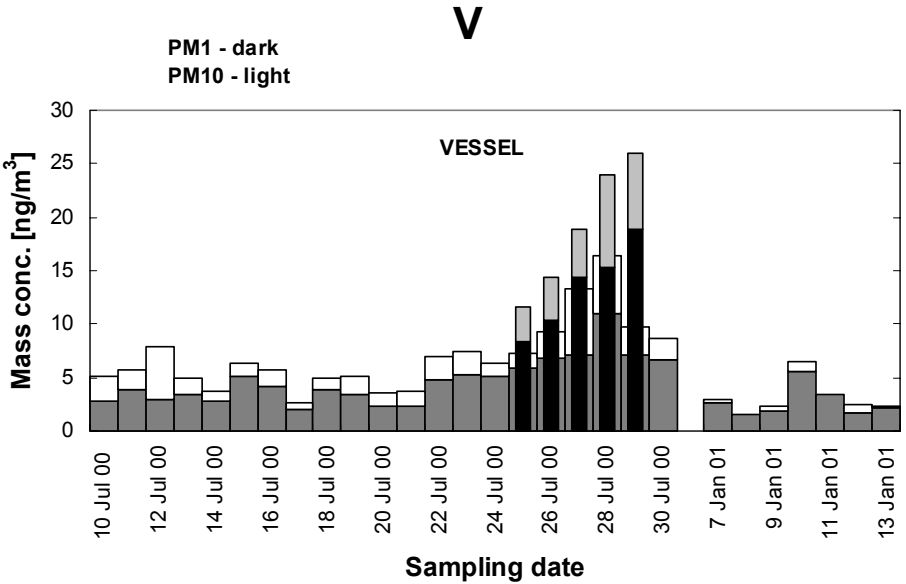

Fig. 3. (e) Continued.

ACPD
3, 2547–2573, 2003

© EGU 2003